

REMARKS

Claims 1 to 21 are all the claims pending in the application.

At page 2 of the Advisory Action of July 28, 2008, the Examiner responds to the arguments applicants submitted in the Response Under 37 C.F.R. § 1.116.

Applicants have reproduced the Examiner's response below, and have added paragraphing and editing for ease of reading.

- (1) The Examiner states as follows:

Applicant argues that Wada's article does not provide data to support his description of "impurity-free, defect-free" particles.

The first [argument] is directed towards a Japanese Patent [filed by Wada] directed towards the same subject matter as that of the [Wada] article. This patent document is, in fact, also directed towards a method of making barium titanate; however, in this patent application, according to what was submitted by the applicant, the method of formation is materially different from the method used [in the] Wada [article].

The Wada [article] uses a low temperature direct synthesis technique, where barium hydroxide and titanium tetrachloride are used at a low temperature. The Japanese patent is directed towards heating barium oxalate tetrahydrate in an oxygen environment followed by several steps.

The steps used in either publication are not [the same], therefore, one cannot argue that the products are the same, and have the same properties.

Furthermore, the applicant cites a paragraph from the Japanese patent stating that the weight loss from the lattice due to hydroxyl groups is as much as 2%. The [patent] document clearly states that the total weight loss over the whole heating range is 2%.

Regardless, the methods in this Japanese [patent] document and that of Wada's [article] use materially different processes to form barium titanate, and thus arguments [based on] the Japanese patent document are moot.

With respect to the Examiner's arguments that the methods in the Wada et al article and the Japanese patent document JP 2003-26423 are not the same, applicants submit that the Examiner is mistaken.

Applicants have previously submitted a computer translation of JP 2003-26423. Applicants now enclose a better translation of this document and an English-language abstract from Patent Abstracts of Japan. Applicants submit that a review of the translation and abstract shows that the same methods are being described in JP 2003-26423 and the Wada et al article.

Applicants first note that the Examiner states that the Wada et al article uses a low temperature direct synthesis technique, where barium hydroxide and titanium tetrachloride are used at low temperature. Applicants cannot find such a description of the use of barium hydroxide and titanium tetrachloride in the Wada et al article.

The Wada et al article describes a two-step thermal decomposition of barium titanyl oxalate comprised of a first step which is a low temperature decomposition of $\text{BaTi}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ (barium oxalate titanyl 4 hydrate) in an oxygen environment, and a second step which comprises annealing the product obtained in the first step in a vacuum at a higher temperature of 550°C to 750°C, such as 620°C for 0.5 hours. This two-step process is the same as described in JP 2003-026423.

As can be seen from the enclosed abstract and translation, including the claims, JP 2003-26423 also discloses a two-step process for producing barium titanate comprised of a first step of heating barium titanyl oxalate tetrahydrate in an oxygen atmosphere at a temperature of 300 to 500°C and a second step of heating the product obtained in the first step in a vacuum at

500°C to 800°C. The heating in the first step can be for 1 to 5 hours, and the heating in the second step can be for 0.5 to 5 hours.

The Wada et al article describes an embodiment of the same method as described in JP 2003-26423, at, for example, page 265, under the heading “The preparation of nm-sized BaTiO₃”

Applicants further point out that the Wada et al article at page 265, right-hand column, states that the particle size of a particle determined by TEM observation and shown in Fig. 3 was 16.5 nm. The Wada et al article indicates that the particle was produced by a two-step process, comprised of a first step wherein BaTi(C₂O₄)₂·4H₂O was annealed for 1 hour in an O₂ flow at a temperature of 400°C, and a second step in which the product from the first step was annealed at 620°C for 0.5 hours in vacuum.

Japanese patent document JP 2003-26423 discloses in paragraphs [0049] and [0050], Table 4, a sample (2) that was produced by heat-treating in a first step a barium titanyl oxalate tetrahydrate at 400°C in O₂ for 1 hour, followed by a second step in which the product of the first step was heat -treated in vacuum at 620°C for 0.5 hours. Paragraphs [0072] and [0076] to [0078] indicate that the particle size of this particle determined by TEM observation was 16.5 nm.

In view of the above, applicants submit that it is clear that the same particles are being described in the Wada et al article and the Japanese patent document JP 2003-26423.

The Examiner also comments on the arguments that applicants submitted relating to paragraphs [0083] to [0085] and [0090] of the Japanese patent. The Examiner states that he

disagrees with applicants' analysis. The Examiner states that the Japanese patent "clearly states that the total weight loss over the whole heating range is 2%."

Paragraphs [0083]-[0085] of JP 2003-26423 do not include a statement that the 2% weight loss by heating in Table 10 is due to removal of hydroxyl groups. However, it is understood from the following descriptions that the 2% weight loss by heating in Table 10 of JP 2003-26423 is due to removal of hydroxyl groups.

With respect to the weight loss by heating in Table 10, the weight was measured with a sample which has adsorbed water on the surface thereof. See paragraph [0085]. Of course, water was adsorbed by the sample and not removed before the measurement, since the sample was not heated before the measurement. Therefore, the weight loss of 2% is considered to be due to removal of hydroxyl groups, rather than removal of adsorbed water.

Next, the 5% weight loss as a whole mentioned in paragraph [0083] of JP 2003-26423 is considered to be the total loss of hydroxyl groups and adsorbed water. Paragraph [0083] states that about half of the 5% weight loss is considered to be due to removal of adsorbed water. Therefore, the rest of the total loss of weight, about 2-3%, is considered to be due to reasons other than the removal of adsorbed water, which is removal of hydroxyl groups.

Thus, applicants submit that it is reasonable to believe from the above descriptions and consideration that the 2% weight loss by heating in Table 10 of JP 2003-26423 is due to removal of hydroxyl groups.

The Wada et al article describes “defect free and impurity free,” but the Japanese Patent document JP 2003-26423, which used the same method as that of the Wada et al article, describes in paragraph [0090] “As a result of characterization of this BaTiO₃ fine particle, the followings have been found: . . . lattice hydroxyl group is less.” In other words, the expression “defect free and impurity free” of the Wada et al article does not mean that it is completely free from defects and impurities.

(2) The Examiner next comments on applicants’ arguments concerning the accuracy of pyncometers as follows:

The second argument is directed towards the density accuracy of pyncometers. The applicant submits that the accuracy of readings by this method is +/- .0001 g/ccm. The Examiner asserts that this error range as cited by applicant is due to mechanical error in the pyncometer, and does not take into account other error as previously stated by the Examiner. Therefore, the arguments applicant submitted that the density of the particles necessitates that the Wada et al article has voids is unconvincing.

Although the Examiner has stated that the error range of +/- 0.0001 g/cc is due to mechanical error in the pyncometer and does not take into account other errors, the Examiner did not provide any evidence or show any basis for this statement.

If the error range of +/- 0.0001 g/cc is due to mechanical error, as the Examiner stated, the “other errors” must be sufficiently small and as small as the range of the mechanical error in the pyncometer (+/- 0.0001 g/cc). The other error ranges should not be as large as a range of 0.1 to 0.01. Otherwise, the high accuracy as a whole cannot be attained.

However, the Wada et al article mentions the values of the densities, 5.78 g/cm^3 and 5.89 g/cm^3 , which include the value of the order of 0.01 and have different values in the order of 0.1 (the difference is 0.11 g/cm^3).

If the accuracy as a whole is in the range of $+/- 0.0001 \text{ g/cc}$, the value of the order of 0.1 cannot be different among the measured values.

Therefore, it is assumed in the Wada et al article that the value of the order of 0.01, at least of the order of 0.1, is discussable, since the value of the order of 0.01 is described.

Thus, the Examiner's view is not based on any evidence or reasoned analysis.

(3) The Examiner has previously relied on the TEM in Fig. 3 in the Wada et al article as supporting his position. Applicants responded by arguing that the TEM in the Wada et al article does not support the Examiner's position. In the Advisory Action, the Examiner responded as follows:

Applicant's third argument is directed towards the TEM image of the particles. Previously, the examiner stated that there were no perturbations in the TEM image. The examiner agrees with the applicant's submission that a perfect single crystal can have voids and defects; however, these voids and defects would be observable in a TEM. TEM is based on the diffraction of an electron beam from crystallographic planes in a sample. Defects such as voids and dislocations perturb the normal diffraction of this beam making such defects observable. These defects are not present in the images provided by [the] Wada [article], which supports the fact that they are not present.

Thus, the Examiner appears to be of the view that since the TEM image in Fig. 3 of the Wada et al article does not show voids and defects, the product of the Wada et al article does not have voids and defects.

However, this view is not correct.

Since the TEM image in Fig. 3 of the Wada et al article shows only a single particle, it is not appropriate to discuss the proportion of particles having voids and defects among the whole particles. From a statistical point of view, only one sample cannot represent all of the samples.

Moreover, if only a few % of particles do not have voids and defects, taking a TEM image of a particle with no voids and defects is not difficult.

As a matter of fact, Fig. 3 of the Wada et al article takes an image with an area of 18 nm x 18 nm. This is too narrow to discuss the voids and defects of particles as claimed in the present invention. If an area of 18 nm x 18 nm is taken out from the image of Fig. 1 of the present application, it is easy to obtain an image of a particle with no voids and defects, although the particles in Fig. 1 are outside the scope of the present invention.

Accordingly, applicants submit that the voids and defects of particles should be discussed by the density and the weight loss by heating, as submitted in applicants' previous argument, and not by a TEM image of a single particle.

As can be seen from the above discussion, the Wada et al article does not disclose or suggest the present invention.

The Wada et al article discloses only barium titanate having a low density and comprising voids, and the process disclosed in the Wada et al article is different from that of the present invention.

Therefore, Wada et al do not defeat the novelty and non-obviousness of the present invention.

In view of the above, applicants submit that Wada et al do not disclose or suggest the subject matter of the present claims. In view of the above, reconsideration and allowance of this application are now believed to be in order, and such actions are hereby solicited. If any points remain in issue which the Examiner feels may be best resolved through a personal or telephone interview, the Examiner is kindly requested to contact the undersigned at the telephone number listed below.

The USPTO is directed and authorized to charge all required fees, except for the Issue Fee and the Publication Fee, to Deposit Account No. 19-4880. Please also credit any overpayments to said Deposit Account.

Respectfully submitted,

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[NAME OF DOCUMENT] Scope of Claim for Patent

[Claim 1] A production method of barium titanate, comprising the following steps:

(a) a first step of heating barium titanyl oxalate tetrahydrate in an oxygen atmosphere, and

(b) a second step of heating the product obtained in said first step, under reduced pressure.

[Claim 2] The production method of barium titanate as claimed in claim 1, wherein the heating temperature in the first step is from 300 to 500°C and the heating temperature in the second step is from 550 to 800°C.

[Claim 3] The production method of barium titanate as claimed in claim 1, wherein the heating temperature in the first step is from 360 to 400°C and the heating temperature in the second step is from 600 to 720°C.

[Claim 4] The production method of barium titanate as claimed in claim 2 or 3, wherein oxygen is flowed in the first step and the pressure is reduced to 10^{-3} Torr or less in the second step.

[Claim 5] The production method of barium titanate as claimed in claim 4, wherein heating in the first step is performed for 1 to 5 hours and the heating in the second step is performed for 0.5 to 5 hours.

[Claim 6] The production method of barium titanate as claimed in claim 5, wherein the average particle size of the product obtained in the second step is from 10 to 100 nm.

[Claim 7] The production method of barium titanate as claimed in claim 6, wherein Ba/Ti of the product obtained in the second step is from 0.98 to 1.02.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to a production method of barium titanate.

[0002]

[Background Art]

A barium titanate particle as a raw material of a multilayered capacitor or an electronic device has been heretofore produced by the following method, which carries with it, however, a problem while particle refinement of raw materials proceeds in the future.

[0003]

First, in the solid phase method, titanium oxide and barium carbonate are weighed and heat-treated at a high temperature of 1,000°C or more to produce a barium titanate particle. This method enables obtaining an impurity-free and defect-free particle but is disadvantageously improper for the production of a fine particle, because due to the reaction at a high temperature, a coarse particle having a particle size on the order of a few μm is produced.

[0004]

Next, in the liquid phase method, the particle is grown in a solution from Ba and Ti ions and the like and therefore, the particle size of a barium titanate particle can be easily controlled to be from a few nm to a few hundreds nm. However, this method has a problem that impurities in the solution, such as hydroxyl group (OH) or hydrocarbon, are also taken into the crystal during production of the barium titanate particle or in terms of the Ba/Ti ratio of the obtained fine particle, the Ba ion necessarily comes short to cause an elevation in the defect concentration. Accordingly, when such a particle is used as the raw material of an electronic device, a texture having a large number of voids in the particle is produced and good electric characteristics cannot be obtained.

[0005]

Next, in the normal thermal decomposition method of barium titanyl oxalate, a barium titanate particle is produced by thermally decomposing barium titanyl oxalate in

air. This method requires a heat treatment temperature of 850°C or more for synthesizing a barium titanate particle. In this method, an impurity-free defect-free barium titanate particle, which is characteristic of the solid phase method, is obtained, but there is a problem that the particle grows to a particle size of at least 150 nm and a fine particle smaller than this particle size cannot be produced. Accordingly, it is expected at present to develop a technique of synthesizing an impurity-free defect-free barium titanate particle having a particle size of 100 nm or less.

[0006]

[Problems to be Solved by the Invention]

As described above, the normal thermal decomposition in air disadvantageously requires a high temperature of 850°C or more because the particle is synthesized through barium carbonate and titanium oxide as intermediate reaction products. Accordingly, a method for synthesizing a barium titanate particle without passing through barium carbonate and titanium oxide as intermediate reaction products must be established.

[0007]

To this end, it is considered that out of conventional methods, the thermal decomposition method of barium titanyl oxalate, which can synthesize an impurity-free defect-free barium titanate particle, needs to be improved and further developed to find a method of producing a barium titanate particle of 10 to 100 nm.

[0008]

The present invention has been made under these circumstances and an object of the present invention is to provide a production method of a barium titanate particle having a particle size of 100 nm or less and having an impurity-free defect-free tetragonal or cubical structure.

[0009]

[Means to Solve the Problems]

The production method of barium titanate of the present invention is a method comprising the following steps: (a) a first step of heating barium titanyl oxalate tetrahydrate in an oxygen atmosphere, and (b) a second step of heating the product obtained in the first step, under reduced pressure.

[0010]

In the production method of barium titanate above, the heating temperature in the first step is from 300 to 500°C and the heating temperature in the second step is from 550 to 800°C. Also, in the production method of barium titanate above, the heating temperature in the first step may be from 360 to 400°C and the heating temperature in the second step may be from 600 to 720°C.

[0011]

In the production method of barium titanate above, oxygen may be flowed in the first step and the pressure may be reduced to 10^{-3} Torr or less in the second step. Also, in the production method of barium titanate above, heating in the first step may be performed for 1 to 5 hours and the heating in the second step may be performed for 0.5 to 5 hours. Furthermore, in the production method of barium titanate above, the average particle size of the product obtained in the second step may be from 10 to 100 nm. In addition, in the production method of barium titanate above, Ba/Ti of the product obtained in the second step may be from 0.98 to 1.02.

[0012]

[Mode for Carrying Out the Invention]

The mode for carrying out the invention of the production method of barium titanate is described below.

[0013]

Based on past studies by the present inventors, it is

known that when barium titanyl oxalate is thermally decomposed in vacuum while exhausting air, the particle size does not increase and a fine barium titanate particle is obtained. However, the obtained barium titanate is not in a tetragonal or cubical structure useful as an electronic material but takes a hexagonal structure. Barium titanate in a hexagonal structure is not useful as an electron material and therefore, it becomes an issue how to obtain a barium titanate particle having a tetragonal or cubical structure by suppressing the production of a hexagonal crystallite.

[0014]

Accordingly, the production mechanism of a hexagonal crystal was studied, as a result, it was found that surplus oxygen is extracted at the desorption of a carbon compound during thermal composition in vacuum and starting from a defect produced due to reduction in the valence from normal tetravalent titanium to trivalent titanium, a hexagonal structure is produced. Then, studies were made to prevent the production of a defect by creating a state having a large amount of oxygen in the atmosphere at the desorption of a carbon compound due to thermal decomposition so as to suppress the production of a defect resulting from change in the valence of titanium and when the thermal decomposition is completed, performing a heat treatment in vacuum while exhausting air.

[0015]

The production method of barium titanate of the present invention comprises the following first and second steps.

[0016]

The first step is described below. The first step is a step of heating barium titanyl oxalate tetrahydrate ($\text{BaTiO}(\text{C}_2\text{O}_4) \cdot 4\text{H}_2\text{O}$, hereinafter referred to as "oxalate hydrate"). Incidentally, the raw material used in the

first step is not limited to this oxalate hydrate. Other examples of the raw material for use in the first step include a mixture of barium and titanium alkoxide.

[0017]

In the first step, oxygen is flowed to create an oxygen atmosphere. The flow rate of oxygen is preferably from 50 to 600 ml/min. The flow rate of oxygen in this range is advantageous in that oxidation is sufficiently performed.

[0018]

The temperature conditions in the first step are described below. In the first step, the temperature is raised at a predetermined rate and thereafter, the system is held at a predetermined temperature for a predetermined time. Subsequently, the temperature is lowered at a predetermined rate. The temperature rise rate is preferably from 1 to 10°C/min. The temperature rise rate in this range is advantageous in that oxidation is sufficiently performed.

[0019]

In the case of holding at a predetermined temperature after the temperature rise, the heating temperature here is preferably from 300 to 500°C. The heating temperature is more preferably from 360 to 400°C. The heating temperature in this range is advantageous in that crystallization of barium carbonate can be suppressed.

[0020]

Also, in the case of holding at a predetermined temperature, the heating time is preferably from 1 to 5 hours. The heating time in this range is advantageous in that crystallization of barium carbonate can be suppressed and at the same time, oxidation is sufficiently performed.

[0021]

After holding at a predetermined temperature, the temperature is lowered at a predetermined rate. The

temperature drop rate is preferably from 1 to 10°C/min. The temperature drop rate in this range is advantageous in that crystallization of barium carbonate can be suppressed. [0022]

The second step is described below. The second step is a step of heating the product obtained in the first step, under reduced pressure. In the second step, the pressure is preferably reduced to 10^{-3} Torr or less. The vacuum degree in this range is advantageous in that the decomposition temperature of barium carbonate can be decreased.

[0023]

The temperature conditions in the second step are described below. In the second step, the temperature is raised at a predetermined rate and thereafter, held at a predetermined temperature for a predetermined time. Subsequently, the temperature is lowered. The temperature rise rate is preferably from 1 to 10°C/min. The temperature rise rate in this range is advantageous in that the decomposition temperature of barium carbonate can be decreased.

[0024]

In the case of holding at a predetermined temperature after the temperature rise, the heating temperature is preferably from 550 to 800°C. The heating temperature is more preferably from 600 to 720°C. The heating temperature in this range is advantageous in that a nm-ordered barium titanate fine particle is obtained.

[0025]

Also, in the case of holding at a predetermined temperature, the heating time is preferably from 0.5 to 5 hours. The heating time in this range is advantageous in that a nm-ordered barium titanate fine particle is obtained.

[0026]

After holding at a predetermined temperature, the

temperature is lowered. The method for lowering the temperature includes two methods, that is, rapid cooling and drop at a predetermined rate. Rapid cooling is advantageous in that an increase in the particle size of the barium titanate fine particle is suppressed.

[0027]

In the case of lowering the temperature at a predetermined rate, the temperature drop rate is preferably from 1 to 10°C/min. The temperature drop rate in this range is advantageous in that the particle size of the barium titanate fine particle can be precisely controlled.

[0028]

The product obtained in the second step is described below. The product obtained in the second step has an average particle size of 10 to 100 nm. When the average particle size is in this range, sintering at a temperature lower by several hundreds °C than that in the case of a normal particle size of 1,000 nm or more is enabled. Alternatively, there is an advantage that the particle can be used as a raw material of a multilayered capacitor.

[0029]

Also, the Ba/Ti ratio of the product obtained in the second step is from 0.98 to 1.02. The Ba/Ti ratio in this range is advantageous in that the original performance as a dielectric can be exerted.

[0030]

In the above-described embodiment, the first step and the second step each is independently performed in terms of temperature rise-holding at a predetermined temperature-temperature drop, but the heating method is not limited thereto. In addition to this, there may also be employed a method where in the first step, the temperature is raised and held at a predetermined temperature; and in the second step, while changing the atmosphere, the temperature is raised to a temperature to be held and after holding at a

predetermined temperature, the temperature is lowered.
[0031]

The present invention is not limited to the above-described embodiments but may, of course, take various other constructions without departing from the gist of the present invention.

[0032]

[Examples]

The present invention is specifically described below by referring to Examples. However, needless to say, the present invention is not limited to these Examples. The production of a fine particle by a 2-step heating method is described here.

[0033]

In this Example, in order to produce a BaTiO_3 fine particle by a 2-step heating method, the following apparatus was produced. That is, in this apparatus, piping for passing a gas to the cover of the sample chamber was installed. In the sample chamber, a thermocouple was fixed so that the temperature of the sample can be measured.

[0034]

In the first step, the flow rate of oxygen was adjusted by a flow meter and the outlet was opened to the atmosphere to keep the sample chamber at atmospheric pressure. In the second step, the sample chamber was evacuated by a vacuum pump and the pressure was confirmed by the Pirani gauge.

[0035]

At the beginning, the first step is described. The purpose here is to examine the substance produced by the heat treatment in oxygen in the first step. The experimental method is described below. In the first step, a commercially available product (trade name: HPBTO-1, produced by Fuji Titanium Industry Co., Ltd.) was used as the oxalate hydrate. This oxalate hydrate has a purity of

99.8 wt%.

[0036]

The oxalate hydrate was weighed and put in a platinum crucible, and an appropriate amount of quartz glass wool was packed therein. While flowing oxygen in an electric furnace, the oxalate hydrate was heat-treated. The temperature rise and temperature drop were performed at 10°C/min, and holding for 1 hour was set. The conditions of holding temperature and flow rate of oxygen in the heat treatment are shown together in Table 1.

[0037]

[Table 1]

Conditions of Heat Treatment in Oxygen

Conditions	Flow Rate of Oxygen (ml/min)	Temperature
(1)	50	365°C
(2)	50	400°C
(3)	100	400°C

[0038]

The difference due to change in the holding temperature was compared by the conditions (1) and (2), and the difference due to change in the flow rate of oxygen was compared by the conditions (2) and (3). After heating, the temperature was allowed to return to room temperature, whereupon the sample was weighed, and the mass change between before and after heating was determined.

[0039]

First, comparison by holding temperature was performed. The calculated mass changes are shown together in Table 2.

[0040]

[Table 2]

Mass Change by Heat Treatment in Oxygen

(Comparison by Holding Temperature)

Conditions	Before Heating (g)	After Heating (g)	Weight Loss (g)	Weight Loss (%)
(1)	3.0072	1.9981	1.0091	33.556
(2)	3.0079	1.9727	1.0352	34.416

[0041]

Taking note of the weight loss (%), the weight loss was larger in (2) with a high temperature than in (1). Also, the weight loss assuming that the oxalate hydrate was completely decomposed into equimolar TiO_2 and BaCO_3 was calculated and found to be 36.020%, which nearly agreed with the weight loss by the heat treatment above. From this, the composition of the sample heat-treated in oxygen is considered to be the same as the equimolar mixture of TiO_2 and BaCO_3 .

[0042]

Next, comparison by the flow rate of oxygen was performed. The calculated mass changes are shown together in Table 3.

[0043]

[Table 3]

Mass Change by Heat Treatment in Oxygen

(Comparison by Flow Rate of Oxygen)

Conditions	Before Heating (g)	After Heating (g)	Weight Loss (g)	Weight Loss (%)
(2)	3.0079	1.9727	1.0352	34.416
(3)	3.0005	1.9633	1.0372	34.568

[0044]

Taking note of the weight loss (%), the weight loss was slightly larger in (3) with a high flow rate of oxygen than in (2). Also in (3), the weight loss after heat

treatment nearly agreed with 36.020% which is a weight loss assuming that the oxalate hydrate was completely decomposed into equimolar TiO_2 and BaCO_3 . From this, the composition of the sample heat-treated in oxygen is considered to be the same as the equimolar mixture of TiO_2 and BaCO_3 .

[0045]

The sample of (3) was further evaluated by XRD and RAMAN to examine the structure. Fig. 1 shows the measurement results by XRD of the sample heat-treated under the condition (3). In the XRD chart, a very broad peak was observed, revealing that the structure is not an orderly structure.

[0046]

Since a crystal structure was not observed from XRD, evaluation by RAMAN spectroscopy was performed to examine the structure in a more microscopic range. This evaluation was performed only for the sample produced under the condition (3). Fig. 2 shows the RAMAN measurement results of the sample heat-treated under the condition (3). In the RAMAN spectrum, only a line as if broad peaks are overlapped was observed, revealing that the sample does not have an orderly structure also in a microscopic range.

[0047]

Summarizing the foregoing, it was found that the heat treatment in oxygen in the first step allows the production of an amorphous having the same composition as the equimolar mixture of TiO_2 and BaCO_3 .

[0048]

The second step is described below. The purpose here is to examine the substance produced by the heat treatment in vacuum in the second step.

[0049]

The experimental method is described below. The sample heat-treated under the condition (3) (flow rate of oxygen: 100 ml/min, 400°C, holding for 1 hour), produced in

the first step above, was used. The sample was weighed and put in a platinum crucible, and an appropriate amount of quartz glass wool was packed therein. After preliminary evacuation, heating in an electric furnace was performed. The temperature was raised at 10°C/min. The conditions of holding temperature and holding time in the heat treatment are shown together in Table 4.

[0050]

[Table 4]

Conditions of Heat Treatment in Vacuum			
Conditions	Temperature	Holding Time (h)	Temperature
(1)	600°C	1	10°C/min.
(2)	620°C	0.5	rapid cooling
(3)	680°C	0.5	rapid cooling
(4)	720°C	0.5	rapid cooling

[0051]

The difference due to cooling conditions was compared by (1) and (2), and the difference due to holding time was compared by (2) to (4). After heating, the temperature was allowed to return to room temperature, whereupon the sample was weighed, and the mass change was determined. The samples all were evaluated by XRD.

[0052]

First, comparison by cooling conditions was performed. Samples all were obtained as a white powder. The mass change in (1) and (2) are shown together in Table 5.

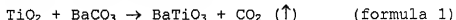
[0053]

[Table 5]

Mass Change by Heat Treatment in Oxygen (Comparison by Flow Rate of Oxygen)				
Conditions	Before Heating (g)	After Heating (g)	Weight Loss (g)	Weight Loss (%)
(1)	0.4997	0.4090	0.0970	18.2
(2)	0.5023	0.4376	0.0647	12.6

[0054]

Taking note of the weight loss (%), the weight loss was larger in (1) with a long holding time. Also, the mass change assuming that the reaction of producing BaTiO₃ from an equimolar mixture of TiO₂ and BaCO₃ (formula 1) was allowed to completely proceed was 15.9%, with which the weight loss of two samples nearly agreed, revealing that BaTiO₃ was produced in both samples.



[0055]

Figs. 3 and 4 show the XRD measurement results of the samples heat-treated under the conditions (1) and (2). In all XRD charts, peaks peculiar to cubic BaTiO₃ as a primary phase and very broad peaks peculiar to hexagonal BaTiO₃ around 26° and 41° as a secondary phase were confirmed, revealing that BaTiO₃ was produced in both samples.

[0056]

Then, the crystallite size was calculated from the half-width of the cubic (111) peak (38° to 40°) in these XRD charts. The calculation of crystallite size used formula 2.

$$\text{Dhkl} = (K\lambda) / (\beta \cos\theta) \quad (\text{formula 2})$$

wherein

Dhkl: crystallite size (m) perpendicular to (hkl)

K: constant 0.9

λ: wavelength (m) of X-ray

β: half-width (rad)

θ: diffraction angle (rad).

[0057]

The half-width was determined from a Gauss curve by fitting a Gauss function to the peak portion of 38° to 40° in the XRD measurement results. Also, the half-width β was obtained by performing optical correction. An external standard method was employed and a powder of SrTiO₃ single

crystal was used for the standard sample. The correction formula is shown in formula (3).

$$\beta = B - b \quad (\text{formula 3})$$

wherein

β : corrected value (rad)

B: measured value (rad) of sample

b: measured value (rad) of standard sample

The calculation results of the crystallite size are shown together in Table 6.

[0058]

[Table 6]

Crystallite Size of Sample Heat-Treated in Vacuum

(Comparison by Holding Time)

Conditions	λ (nm)	β (10^{-3} rad)	Diffraction Angle ($^{\circ}$)	D_{111} (nm)
(1)	0.1541	8.025	19.33	18.31
(2)	0.1542	8.832	19.33	16.64

[0059]

Taking note of the crystallite size D_{hkl} , the sample of (2) has a finer crystallite size and it was revealed that a BaTiO_3 fine particle can be more finely produced in (2) with a short holding time. This is considered to result because the sample is not present for a long time in a temperature region allowing for nuclear growth.

[0060]

Then, Comparison by the holding temperature was performed. In all cases, a white powder was obtained. The mass changes in the conditions (2), (3) and (4) are shown together in Table 7.

[0061]

[Table 7]

Mass Change by Heat Treatment in Vacuum

(Comparison by Flow Rate of Oxygen)

Conditions	Before Heating (g)	After Heating (g)	Weight Loss (g)	Weight Loss (%)
(2)	0.5023	0.4376	0.0647	12.6
(3)	0.5045	0.4398	0.0656	13.0
(4)	0.5027	0.4364	0.0663	13.2

[0062]

Taking note of the weight loss (%), as the holding temperature is higher, the weight loss is found to be slightly larger. Also, the mass change assuming that the reaction of producing BaTiO_3 from an equimolar mixture of TiO_2 and BaCO_3 was allowed to completely proceed was 15.9%, to which the weight loss of three samples was almost similar, revealing that BaTiO_3 was produced in all samples. A higher holding temperature is considered to allow for more proceeding of the reaction.

[0063]

Figs. 4 to 6 show the XRD measurement results of the samples heat-treated under the conditions (2) to (4). In all XRD charts, peaks peculiar to cubic BaTiO_3 as a primary phase and very broad peaks peculiar to hexagonal BaTiO_3 around 26° and 41° as a secondary phase were confirmed. Also, it is seen that as the holding temperature is higher, the peak of the hexagonal crystal tends to become broader. A high holding temperature is found to be effective for the removal of a hexagonal crystal.

[0064]

Then, the crystallite size was calculated from the half-width of the cubic (111) peak (38° to 40°) in these XRD charts. The calculation of crystallite size used formulae 2 and 3. The calculation results of the crystallite size are shown together in Table 8.

[0065]

[Table 8]

Crystallite Size of Sample Heat-Treated in Vacuum

(Comparison by Holding Temperature)

Conditions	λ (nm)	β (10^{-3} rad)	Diffraction Angle ($^{\circ}$)	D_{111} (nm)
(2)	0.1542	8.832	19.33	16.64
(3)	0.1542	8.919	19.36	16.48
(4)	0.1542	6.625	19.40	22.19

[0066]

Taking note of the crystallite size D_{hkl} , the crystallite size was largest in (4) with a highest holding temperature and was almost the same in (2) and (3). Since the crystallite size has temperature dependency, it is considered that the $BaTiO_3$ fine particle produced by this 2-step heating method has sinterability.

[0067]

Summarizing the foregoing, it was found that the sample which was amorphous in the first step is crystallized by the heat treatment in vacuum and $BaTiO_3$ having a crystallite size of 17 to 25 nm can be produced by the 2-step heating method. The crystal structure was almost cubic $BaTiO_3$, and hexagonal $BaTiO_3$ was very little confirmed.

[0068]

These results reveal that a $BaTiO_3$ fine particle can be produced by a 2-step heating method. Accordingly, it was decided to further perform the characterization of this $BaTiO_3$ fine particle.

[0069]

The experimental method is described here. In the evaluation, RAMAN, TEM, IR, TG-DTA and BET were used. The evaluation methods and samples are shown together in Table 9. The sample number and condition conform to those in Table 4. Samples of the conditions (2), (3) and (4) in

Table 4 were used.

[0070]

[Table 9]

Evaluation Method and Sample		
	Evaluation Method	Sample
RAMAN	(fine crystal structure)	(2) (3) (4)
TEM	(aggregated state and particle size)	(2)
IR	(impurities)	(2) (3) (4)
TG-DTA	(impurities)	(2)
BET	(surface area)	(2)

[0071]

The evaluation results are described below. Figs. 7 to 9 show the Raman spectra of (2), (3) and (4). In all spectra, peaks of cubic BaTiO_3 and hexagonal BaTiO_3 can be confirmed. Furthermore, as the holding temperature is higher, the peak of hexagonal BaTiO_3 tends to become broader, which agrees with the results of XRD. It is also seen from these that a higher holding temperature is effective for the removal of hexagonal BaTiO_3 .

[0072]

Figs. 10 and 11 each is a TEM photograph when the particle of (2) is observed. From the TEM observation, a particle regarded as hexagonal BaTiO_3 is not found.

[0073]

In Fig. 10, a state of some particles being overlapped is observed. A distinct grain boundary is not observed between a particle and a particle, nevertheless, a gap is also not present, which suggests that particles are aggregated by a significantly strong force.

[0074]

Fig. 11 shows a particle in a state of being dispersed into only one particle. A clear lattice plane

can be observed and this has one direction, which suggests that the particle is a single crystal particle. The number of lines for the lattice plane was 41.

[0075]

This particle was subjected to electron beam diffraction, as a result, clear spots as shown in Fig. 12 were observed. The arrangement of these spots reveals that this lattice plane is (001) of face-centered structure. From these, the lattice plane is considered to be cubic (001).

[0076]

Assuming that the sample (2) is a cubic crystal, the lattice constant was determined from (111) peak of the XRD measurement results, and the particle size of $\langle 001 \rangle$ of the particle in Fig. 11 was calculated from the lattice constant and the number of (001). The lattice constant of (2) was 0.4031 nm, and the number of lines for the lattice plane was 41.

[0077]

(Lattice constant ((001) plane spacing) \times (number of lattices) = $0.4031 \times 41 = 16.53$.

[0078]

Thus, the particle size of this particle was 16.5 nm. The particle size determined is almost similar to the crystallite size of (2) in Table 8, which also suggests that the particle is a single crystal particle.

[0079]

Figs. 13 to 15 show the IR spectra of (2), (3) and (4). Also, for the purpose of comparison, Fig. 16 shows the IR spectrum of a commercially available BaTiO_3 fine particle (trade name: BT01, produced by Sakai Chemical Industry Co., Ltd.) having a particle size of about 100 nm, which is synthesized by a hydrothermal technique.

[0080]

In all spectra, an absorption peak is observed around

1,500 cm^{-1} and 3,500 cm^{-1} . These are absorption of carbonic acid group and hydroxyl group. The absorption of carbonic acid group is considered to result from carbonation of the surface. The absorption is smallest in the commercially available fine particle. In the samples by the 2-step heating method, as the holding temperature in the heat treatment is lower, the peak becomes sharper, which suggests that as the holding temperature is lower, the surface area is larger.

[0081]

Taking note of the absorption of hydroxyl group, the peak is broad in all samples produced by the 2-step heating method. On the other hand, the commercially available fine particle gives a sharp peak, which is considered because a lattice hydroxyl group is present. The lattice hydroxyl group, where the oxygen and hydrogen positions are fixed, is limited in the oscillation and gives a sharp peak. On the other hand, the broad peak is attributable to adsorbed water and since the oscillation is relatively free as compared with the lattice hydroxyl group, the peak becomes broad.

[0082]

Also, comparing between fine particles by the 2-step heating method, as the holding temperature is higher, the peak of hydroxyl group is broader. This is considered to occur because as the holding temperature is higher, the surface area becomes small and adsorbed water is reduced.

[0083]

Sample (2) was subjected to measurement of TG-DTA. The sample was heated at 10°C/min from room temperature to 1,000°C and air was flowed into the sample chamber. Fig. 17 shows the measurement results. The TG curve shows abrupt weight loss around 100°C, and gradual weight loss is observed between 400°C and 600°C. The entire weight loss was about 5%. The results when the mass change between

before and after measurement at room temperature was calculated are shown together in Table 10.

[0084]

[Table 10]

Mass Change by TG-DTA			
Before Heating (g)	After Heating (g)	Weight Loss (g)	Weight Loss (%)
0.0354	0.0346	0.008	2%

[0085]

There is a great difference between the weight loss (%) after measurement in Fig. 17 and the weight loss (%) in Table 10. It is considered that in the case of the mass change at room temperature, since the mass is weighed at room temperature after heating, water is adsorbed to the surface, as a result, the mass becomes larger than the mass at 1,000°C of TG-DTA. Also, the fine particle is thought to undergo grain growth during heating in the TG-DTA measurement, and about half of the weight loss of TG-DTA is estimated to be attributable to adsorbed water.

[0086]

Measurement of surface area by BET was performed. Preliminary degassing was performed at 150°C for 2.5 hours. Nitrogen was used for the adsorption gas. As a result of the measurement, the surface area was 22.24 m²/g.

[0087]

From the results of characterization of the above-described BaTiO₃ fine particle, the advantages of the fine particle produced by the 2-step heating method are summarized below. Hexagonal BaTiO₃ is present but tends to decrease as the holding temperature is higher, and the fine particle has potential as a raw material of a sintered body. The particle is a single crystal particle and is a fine particle having a small particle size. Also, since a liquid phase is not passed through at the reaction, the

lattice hydroxyl group is less allowed. In this way, the 2-step heating method is verified to be effective for the production of a good-quality fine particle.

[0088]

The summary of this Example is as follows. The 2-step heating method of this Example is a method of first applying a heat treatment at a low temperature in oxygen and then applying a heat treatment at a high temperature in vacuum. In the first step, heat treatment in oxygen is performed, whereby remaining of C and the resultant reducing atmosphere are prevented. Mixing on an atomic scale is aimed so that Ti and Ba can be more closely arranged. In the second step, heat treatment is performed in vacuum while exhausting air to examine whether by reducing the CO₂ partial pressure, BaTiO₃ can be produced while preventing the production of BaCO₃.

[0089]

As a result of experiments, it has been found that: in the first step, an amorphous having the same composition as an equimolar mixture of TiO₂ and BaCO₃ is produced by the heat treatment in oxygen, and in the second step, the sample which is amorphous in the first step is crystallized; and BaTiO₃ having a crystallite size of about 17 to 25 nm can be produced by the 2-step heating method. The crystal structure is almost cubic BaTiO₃, though hexagonal BaTiO₃ is slightly confirmed.

[0090]

As a result of characterization of this BaTiO₃ fine particle, the followings have been found: hexagonal BaTiO₃ is present but tends to decrease as the holding temperature is higher and the produced particle is a single crystal particle having potential as a raw material of a sintered body; and since a liquid phase is not passed through at the reaction, the lattice hydroxyl group is less allowed. In this way, the 2-step heating method is effective for the

production of a good-quality fine particle.

[0091]

[Effects of the Invention]

The present invention provides the following effects. As a result of development of a 2-step thermal decomposition method of barium titanyl oxalate, synthesis of a barium titanate fine particle having a cubic structure has succeeded. Also, the obtained barium titanate fine particle has no impurities inside of the particle and the obtained Ba/Ti ratio is also almost 1, confirming that a defect-free particle can be obtained. Furthermore, this barium titanate fine particle abruptly undergoes grain growth at 720°C or more and therefore, a barium titanate ceramic or ceramic film can be obtained at 1,000°C or less. Accordingly, in a ceramic process where baking is conventionally performed at 1,200°C or more, energy can be saved and the apparatus can be downsized. Also from these standpoints, this barium titanate fine particle has potential as a raw material of future multilayered capacitors or electronic devices.

[Brief Description of the Drawings]

[Fig. 1] A view showing the XRD profile when oxalate hydrate is heat-treated at 400°C in oxygen.

[Fig. 2] A view showing the RAMAN spectrum when oxalate hydrate is heat-treated at 400°C in oxygen.

[Fig. 3] A view showing the XRD profile when oxalate hydrate is heat-treated at 400°C in oxygen and then heat-treated at 600°C in vacuum for 1 hour.

[Fig. 4] A view showing the XRD profile when oxalate hydrate is heat-treated at 400°C in oxygen and then heat-treated at 620°C in vacuum for 0.5 hours.

[Fig. 5] A view showing the XRD profile when oxalate hydrate is heat-treated at 400°C in oxygen and then heat-treated at 680°C in vacuum for 0.5 hours.

[Fig. 6] A view showing the XRD profile when

oxalate hydrate is heat-treated at 400°C in oxygen and then heat-treated at 720°C in vacuum for 0.5 hours.

[Fig. 7] A view showing the RAMAN spectrum when oxalate hydrate is heat-treated at 400°C in oxygen and then heat-treated at 620°C in vacuum for 0.5 hours.

[Fig. 8] A view showing the RAMAN spectrum when oxalate hydrate is heat-treated at 400°C in oxygen and then heat-treated at 680°C in vacuum for 0.5 hours.

[Fig. 9] A view showing the RAMAN spectrum when oxalate hydrate is heat-treated at 400°C in oxygen and then heat-treated at 720°C in vacuum for 0.5 hours.

[Fig. 10] A TEM photograph showing the aggregated state of a fine particle product obtained when oxalate hydrate is heat-treated at 400°C in oxygen and then heat-treated at 620°C in vacuum for 0.5 hours.

[Fig. 11] A TEM photograph showing the particle state of a product obtained when oxalate hydrate is heat-treated at 400°C in oxygen and then heat-treated at 620°C in vacuum for 0.5 hours.

[Fig. 12] A view showing the electron beam diffraction pattern of a fine particle product obtained when oxalate hydrate is heat-treated at 400°C in oxygen and then heat-treated at 620°C in vacuum for 0.5 hours.

[Fig. 13] A view showing the IR spectrum when oxalate hydrate is heat-treated at 400°C in oxygen and then heat-treated at 620°C in vacuum for 0.5 hours.

[Fig. 14] A view showing the IR spectrum when oxalate hydrate is heat-treated at 400°C in oxygen and then heat-treated at 680°C in vacuum for 0.5 hours.

[Fig. 15] A view showing the IR spectrum when oxalate hydrate is heat-treated at 400°C in oxygen and then heat-treated at 720°C in vacuum for 0.5 hours.

[Fig. 16] A view showing the IR spectrum of a commercially available fine particle synthesized by a hydrothermal technique.

[Fig. 17] A view showing the TG-DTA curve of a product obtained when oxalate hydrate is heat-treated at 400°C in oxygen and then heat-treated at 620°C in vacuum for 0.5 hours.

FIG. 1

XRD PROFILE

HEAT TREATMENT OF OXALATE HYDRATE AT 400°C IN OXYGEN

FIG. 2

RAMAN SPECTRUM

HEAT TREATMENT OF OXALATE HYDRATE AT 400°C IN OXYGEN

FIG. 3

XRD PROFILE

HEAT TREATMENT IN OXYGEN → IN VACUUM AT 600°C FOR 1 HOUR
TEMPERATURE RISE: 10°C/MIN

FIG. 4

XRD PROFILE

HEAT TREATMENT IN OXYGEN → HEAT TREATMENT IN VACUUM AT
620°C FOR 0.5 HOURS

FIG. 5

XRD PROFILE

HEAT TREATMENT IN OXYGEN → IN VACUUM AT 680°C FOR 0.5
HOURS

FIG. 6

XRD PROFILE

HEAT TREATMENT IN OXYGEN → IN VACUUM AT 720°C FOR 0.5
HOURS

FIG. 7

RAMAN SPECTRUM

HEAT TREATMENT AT 620°C IN VACUUM FOR 0.5 HOURS

FIG. 8

RAMAN SPECTRUM

HEAT TREATMENT AT 680°C IN VACUUM FOR 0.5 HOURS

FIG. 9

RAMAN SPECTRUM

HEAT TREATMENT AT 720°C IN VACUUM FOR 0.5 HOURS

FIG. 10

TEM PHOTOGRAPH

AGGREGATED STATE

FIG. 11

TEM PHOTOGRAPH

PARTICLE STATE

FIG. 12

ELECTRON BEAM DIFFRACTION PATTERN OF FINE PARTICLE

FIG. 13

IR SPECTRUM

HEAT TREATMENT AT 620°C IN VACUUM FOR 0.5 HOURS

FIG. 14

IR SPECTRUM

HEAT TREATMENT AT 680°C IN VACUUM FOR 0.5 HOURS

FIG. 15

IR SPECTRUM

HEAT TREATMENT AT 720°C IN VACUUM FOR 0.5 HOURS

FIG. 16

IR SPECTRUM

COMMERCIALY AVAILABLE PRODUCT (SYNTHESIZED BY HYDROTHERMAL
TECHNIQUE)

FIG. 17

TG-DTA CURVE

2-STEP HEATING METHOD (AT 400°C IN OXYGEN → AT 620°C IN
VACUUM)

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-026423

(43)Date of publication of application : 29.01.2003

(51)Int.Cl.

C01G 23/00
C04B 35/626

(21)Application number : 2001-209516

(71)Applicant : RIKOGAKU SHINKOKAI

(22)Date of filing : 10.07.2001

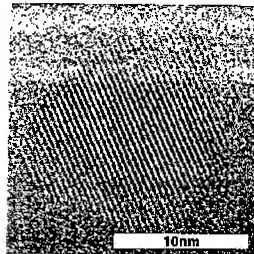
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(54) METHOD FOR PREPARING BARIUM TITANATE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for preparing barium titanate particles with ≤ 100 nm particle diameter without any impurities or any defects.

SOLUTION: The method for preparing barium titanate comprises the first step of heating barium titanyl oxalate tetrahydrate in an atmosphere of oxygen and the second step of heating a product obtained with the first step under reduced pressure. The heating temperature in the first step is in $300\text{--}500^\circ\text{C}$ range and the heating temperature in the second step is in $550\text{--}800^\circ\text{C}$ range. Also oxygen is made to flow in the first step and the pressure is reduced to $\leq 10^{-3}$ Torr in the second step. The average particle diameter of a product obtained with the second step is in $10\text{--}100$ nm range.



TEM写真 粒子状態